

In Situ Electrochemical Generation of Ferrate for Water Treatment

Presentation to 215th Electrochemical Society Meeting

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May 27, 2009
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Motivation

- Reactive innovations is a small business focused on developing electrochemical technologies such as : electrolysis, fuel cells, reactive separations, advanced water treatment eactive innovations is a small business locused on developing electrocriemical
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eatment
for next generation are prompting new innovations
- Environmental regulation are prompting new innovations in water treatment
- In the future, both centralized and decentralized water treatment must avoid the use of chlorine
- This work came about because of the Navy's need for onboard waste water processing treatment which resulted in a research and development program
	- focused mission capability and facilitate technology refresh.
- Fraction and the future, both centralized and decentralized water treatment must avoid the use

f chlorine

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Wastewater Processing options

- Wastewater Processing options

Current commercial technologies include biological, physical/chemical and advanced oxidation

 Require large tanks treatments Wastewater Processing option

University commercial technologies include biological, physical/chemical

Leatments

- Require large tanks

- Not tested with high levels of contaminants

- Typically not rapid-start systems. Wastewater Processing options

United Statements

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United Statements

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- Nedure large tanks

 Not tested with high levels of contaminants

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 Advanced technologies must also be incompliance with EPA to limit discharge of contaminated

waste streams into environmental requirements: ferrate

and intervironmental requirements

and various dechange of contain

and variable states and the state is acceptable levels

• Process must reduce contaminants to acceptable levels

•

Ferrate background

- **Ferrate backgrou**

What is Ferrate?

 Iron in its familiar form exists in the +2 and +3 valence state

 Higher valence states are generated as oxyanions of iron

 iron in the +6 state is FeO₄²also called ferrate

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	-
- Ferrate background

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 – FeO₄⁻² + 8H⁺ + 3e⁻ → Fe⁺³ + 4H₂O
– FeO₄⁻² + 4H₂0 +3e⁻ → Fe⁺³ + 8OH⁻
- Ferrate background

sts in the +2 and +3 valence state

generated as oxyanions of iron
 $\frac{2,2}$ also called ferrate

determined in both acidic and basic media

+4H₂O

= $\frac{E_o = +2.2 \text{ V}}{E_o = +0.72 \text{ V}}$

= $\frac{E_o = +0.72 \text$ **Ferrate background**

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betentials have been determi Ferrate background

The states are generated as oxyanic state

to state is FeO_4^2 also called ferrate

of state is FeO_4^2 also called ferrate

Is have been determined in both acidic and basic media
 $+3e^- \rightarrow Fe^{*3} + 4H_2$ Ferrate background
 $=$ - Iron in its familiar form exists in the +2 and +3 valence state
 $=$ Higher valence states are generated as oxyanions of iron
 $=$ FoQ₄² + 8H + 3 \rightarrow Fe⁰³ + 4H₂O \leq also called ferra **Ferrate background**

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FeO₄² **Effectiveness of Ferrates in the stationary of Ferrates in the stationary of Ferrates in the other stations of Ferrate Redict Section Associated formet and the stations of Ferrate packets are performed in both acidic and** Ferrate background

That is Ferrate?

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— Iron in the 45 atte is FoQ-²48 colled ferrate

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— iron in the +6 **FEITALE DACK

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- iron in the +6 state is FeO₄⁻² also called ferrate

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- Ferrate is self- the state is self- removing a bend to the state of the mind the state is self- $\frac{1}{2}$ and $\frac{1}{2}$ and Is Ferrate?

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iH⁺ + 3e⁻ → F form exists in the +2 and +3 valence state

ates are generated as oxyanions of iron

e is FeO₄²-also called ferrate

ve been determined in both acidic and basic media

→ Fe⁺³ + 4H₂O

→ Fe⁺³ + 8OH·

E₀ = +2.2
- Iron in ts familiar form exists in the +2 and +3 valence state

 Irigher valence states are generated as oxyanions of iron

 iron in the +6 state is FeO₄⁻²also called ferrate

 $F \in O_4^{2+}$ sH⁺ 3e' \rightarrow Fe⁺³ Higher valence states are generated as oxyanions of iron

iron in the +6 state is FeO₄²-also called ferrate

x potentials have been determined in both acidic and basic media

FeO₄²⁺ a Bi+ + 3e → Fe⁺³ + 8H₁O

F From in the +6 state is FeO₄^{-z}also called ferrate

Redox potentials have been determined in both acidic and basic media
 $E_c = +2.2 \text{ V}$ (1)

FeO₄²+ 8H⁺ 3-8⁻ → 5F⁹³+8H₂O

Ferrate species is perhass the most procedures = FeO₄² + 8H⁺ + 3e⁻ → Fe³ + 4H₂O

= FeO₄² + 4H₂O + Fe³ + 4H₂O

= Ferrate species is perhaps the most powerful oxidizing compound that can be

applications with a higher potential in acid media than – Fo $Q_*^2 + 4H_10 \cdot 39 \cdot \rightarrow$ Fe³⁺ 80H+ Both control E_g = 40.72 V
Ferrate species is perhaps the most powerful oxidizing compound that can be used in normal
applications with a higher potential in acid media than either – Ferrate is precise is the meast produced in highly compound that can be used in normal
splications with a higher potential in acid media than either ozone (2.04V) or chlorine ~1.4 V)

Effectiveness of Ferrates in treati applications with a higher potential in acid media than either ozone (2.04V) or chlorine ~1.4 V)

dependent of Ferrates in treating wastewater has been well reported:

- Removes toxic organic ions such as cyanide

- Destro Effectiveness of Ferrates in treating wastewater has been well reported:

- Removes toxic organic lons such as cyanide

- Destroys viruses

- Destroys viruses

- Destroys bacteria

errate is self-removing and produces a b
- -
	-
	-
	-
- $4 -$ Expensive process to stabilize the end product
— Commercial attempts to generate reasonably priced ferrate compounds have failed to date

Reactive Innovations, LLC

Our Technical Approach

- In Situ Electrochemical Generation of Ferrate
- **Our Technical Approach

A Situ Electrochemical Generation of Ferrate

 Generate and use ferrate in a flowing electro-oxidation

decontamination reactor

Eliminates stability issue** decontamination reactor **Our Technical Approach

The Situ Electrochemical Generation of Ferrate

- Generate and use ferrate in a flowing electro-oxidation

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- lifetime of ferrate in aqueous solu Our Technical Approach

fu Electrochemical Generation of Ferrate

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fetime of ferrate in aqueous solutions has been me**
- **•** Eliminates stability issue
	- -
		-
- **Our Technical Approach**

tu Electrochemical Generation of Ferrate

Senerate and use ferrate in a flowing electro-oxide

econtamination reactor

inates stability issue

fetime of ferrate in aqueous solutions has been r

 • Our approach does not regard ferrate as a long-lived bulk chemical but as a transient electrochemically mediating species
- By producing and consuming ferrate in the same reactor, the required lifetime will not necessitate a high pH

Electrochemical Generation of Ferrate

- Ferrate can be electrochemically generated using iron metal or ferric oxide in both alkaline and acid media: **Electrochemical Generatio**

Firate can be electrochemically generated u

xide in both alkaline and acid media:

Ikaline media

- ferric oxide starting material:

• Anode : $0.5(Fe_2O_3-H_2O) + 5OH^- \rightarrow FeO_4^{-2} + 3H_2O$

• Cathod **Electrochemical Generation (**
te can be electrochemically generated using
in both alkaline and acid media:
ine media
arric oxide starting material:
• Anode: $0.5(Fe_2O_3+H_2O) + 5OH^- \rightarrow FeO_4^{-2} + 3H_2O + 3$
• Cathode: $3H_2O + 3$ **Electrochemical Generation of Ferrate**
te can be electrochemically generated using iron metal or fe
in both alkaline and acid media:
ine media
stric oxide starting material:
• Anode: $0.5(Fe_2O_3\text{-}H_2O) + 5OH\text{-} \rightarrow FeO_4{}^2$ **Electrochemical Generatio**

errate can be electrochemically generated u

xide in both alkaline and acid media:

lkaline media

- ferric oxide starting material:

• Anode: 0.5(Fe₂O₃-H₂O) + 5OH· → FeO₄² +3H₂

• Electrochemical Generation of Ferrate

te can be electrochemically generated using iron metal or

in both alkaline and acid media:

ine media

ine media

• Anode: 0.5(Fe₂O₃-H₂O) + 5OH⁻ → FeO₄²+3H₂O + 3e·

• Electrochemical Generation of Ferrate

te can be electrochemically generated using iron metal or f

in both alkaline and acid media:

ine media

rric oxide starting material:

• Anode: 0.5(Fe₂O₃-H₂O + 30H + H₂

ca For the case of the electrochemically generated units

starting material:
 $\frac{1}{1}$ labeline media
 $\frac{1}{2}$ ferric oxide starting material:
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 $\frac{1}{2}$ for $\frac{1}{2}$ ferric oxi te can be electrochemically generated using iron m

in both alkaline and acid media:

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erric oxide starting material:

• Anode: $0.5(Fe_2O_3-H_2O) + 5OH \rightarrow FeO_4^2 + 3H_2O + 3e$

• Cathode: $3H_2O + 3e \rightarrow 3OH + H_2$

on metal te can be electrochemically generated using iron metal or

in both alkaline and acid media:

ine media

iric oxide starting material:

• Anode: $0.5(Fe_2O_3 \cdot H_2O) + 5OH \rightarrow FeO_4^2 \cdot 3H_2O + 3e$

• Cathode: $3H_2O + 3e \rightarrow 3OH + H_2$

- Alkaline media
	- - $-H_2O$) + 5OH $\cdot \rightarrow FeO_4^{-2}$ +3H $_2$ 0 + 3e \cdot
		-
	- -
		-
- Acid/neutral environment:
	- - $-H_2O$) + 2 $H_2O \rightarrow FeO_4^{-2}$ +5H⁺ + 5e⁻
		- Cathode $5H^+$ +5e \rightarrow 3H₂
- In our approach, electrochemically produced ferrate oxidizes contaminants and is reduced to an iron species Here is the contribution of the carbon distribution of the carbon distribution of the carbon distribution of the sole of th • Anode: 0.5(Fe₂O₃-H₂O) + 5OH· → FeO₄² +3H₂O + 3
• Cathode: 3H₂O + 3e· → 3OH· + H₂
• Cathode: 3H₂O + 3e· → 3OH· + H₂
• Anode: Fe+ 8OH· → FeO₄² +4H2O + 6e·
• Cathode: 6H₂O + 6e·→ 6OH·+3H₂
neut
	- - $FeO₄$ ⁻² + CH₃OH \rightarrow Fe(OH)₃ + CO₂ + 2OH-

Tubular Decontamination Reactor

based on RIL micro-tubular manufacturing technology

Reactive Innovations, LLC

Electrochemical Decontamination Reactor

- •Incorporates a packed bed anode •Iron or iron oxide
- •Wastewater flows through the packed bed
- •Voltage is applied
- •Ferrate is generated
- •Ferrate reacts with contaminants

- Chemical Oxygen Demand: primary indicator of phase I reactor effectiveness Analysis methods

Shemical Oxygen Demand: primary indicator of phase I reactor

Ffectiveness

- Measured in house using EPA-approved colorimetric method

- BioScience Accutest COD test kit

- Thorstensen Analytical Laborat Analysis methods

inical Oxygen Demand: primary indicator of phase I reac

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• EPA approved H Analysis methods

Unemical Oxygen Demand: primary indicator of phase

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horstensen Analytical Laboratory
• EPA approved Hach 9000
hemical oxygen d
	- -
	- -
- Biochemical oxygen demand
	-
	- -
- Fecal Coliform
- Measured in house using EPA-approved colorimetric meth

 BioScience Accutest COD test kit

 Thorstensen Analytical Laboratory

 EPA approved Hach 9000

Biochemical oxygen demand

 Estimated in house by COD/BOD ratio

Initial Single Tube MEA Test Reactor

Test progression

- 1. Produced ferrate in 4 M NaOH, pH>14
- 2. Processed simulated laundry wastewater $pH = 9$
- 3.Processed graywater using Navy recipe pH= 7

(Diluted graywater simulant to obtain initial COD values in desired range)

4. Processed blackwater from municipal treatment facility

4 Tube Array Processing graywater

4 Tube Array Processing graywater (continued)

- As expected 4 tube array processes volume of wastewater much faster 4 Tube Array

Processing graywater (continued)

So expected 4 tube array processes volume of wastewater

Time to reduce COD from 2500 to 1500 mg/ l is ~ 10 hours in

single tube and less than 0.5 hour in 4 tube array
	- single tube and less than 0.5 hour in 4 tube array
- COD decrease is non-linear with time. Most of the decrease occurs in the first few hours. Potential causes for plateau in performance: Solution of anode. Production of the ferric oxide (rust) in Section of the ferric oxide (rust) in single tube and less than 0.5 hour in 4 tube array

COD decrease is non-linear with time. Most of the decrease

ccurs in th is expected 4 tube array processes volume of wastewater

Time to reduce COD from 2500 to 1500 mg/ l is ~ 10 hours in

single tube and less than 0.5 hour in 4 tube array

COD decrease is non-linear with time. Most of the de
	- ferrate production
	- ferric/ferrous ions. Possible interference in COD and BOD analysis.

4 Tube Array Processing 5 liters of graywater

Processing time scales with volume

(factor of 8.3): In this test COD values drops from ~1500 to 700 in 8 hours compared to 600 ml test where the same drop occurred in less than 1 hour.

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4 tube array

Volume:600 ml

Cell conditions: 2.7 V, 7.5 Amps

Wastewater sample: Lowell Regional wastewater facility Primary effluent

- Demonstrated *in situ* production of ferrate in pH neutral wastewater
- Ferrate Reactor Summary

 Demonstrated *in situ* production of ferrate in pH neutral

wastewater

 Demonstrated decontamination of simulated graywater and

 Best phase I results for graywater blackwater Ferrate Reactor Summar

Demonstrated *in situ* production of ferrate in p

vastewater

Demonstrated decontamination of simulated g

lackwater

- Best phase I results for graywater

- 33% COD removal,

- 70% BOD removal Ferrate Reactor Summa

interaction of ferrate in

ewater

interaction of simulated

stater

For gast phase I results for graywater

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For gast phase I results for blackwater

For gast phase I results f Ferrate Neactor Summa

ionstrated *in situ* production of ferrate in

ewater

onstrated decontamination of simulated

sest phase I results for graywater

• 93% COD removal

lest phase I results for blackwater

• 89 % COD r – Demonstrated *in situ* production of ferrate in planet

– Demonstrated decontamination of simulated g

– Best phase I results for graywater

– 93% COD removal,

– 70% BOD removal

– Best phase I results for blackwater
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stest phase I results for graywater
• 93% COD removal,
est phase I results for blackwater
• 89 % COD removal,
• 53% BOD removal
• 9 onstrated *in situ* production of ferrate in pH neut

ewater

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est phase I results for graywater

• 93% COD removal,

• 70% BOD removal

est phase I results for blackwater

• 89 % COD removal,

• 53% BOD removal

• 98 % Fecal
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